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# Removal of Fluorides from Industrial Wastewaters Using Activated Alumina

Feldspar Corp.
Spruce Pine, NC

Prepared for

Industrial Environmental Research Lab.
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# REMOVAL OF FLUORIDES FROM INDUSTRIAL WASTEWATERS USING ACTIVATED ALUMINA

by

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Grant No. R-804377

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This report has been reviewed by the Industrial Environmental Research Laboratory - Cincinnati, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

## FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution contol methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is a product of the above efforts. These studies were undertaken to perform a laboratory-scale investigation to remove excess concentrations of fluoride ion from wastewaters emanating from plants that separate feldspar from ore by wet-process methods. The fluoride removal process is specifically directed to the wastewaters from the feldspar-sand froth flotation step.

Such information will be of value both to EPA's regulatory program (Effluent Guidelines Division) and to the industry itself in arriving at meaningful and achievable discharge levels. Within EPA's R&D program, the information will be used as part of the continuing program to develop and evaluate improved and less costly technology to minimize industrial waste discharges.

For further information concerning this subject, the Metals and Inorganic Chemicals Branch should be contacted.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

## ABSTRACT

A four-step, bench-scale process has been developed that is capable of removing at least 92 percent of the soluble fluoride from feldspar flotation process wastewaters at a projected cost of $1.03/kkg ($0.93/ton) of feldspar. For a 163,000 kkg/year (180,000 ton/year) plant, the initial capital expenditure would be about $200,000. The wastewater is pretreated with sodium hydroxide, lime, and calcium chloride, which removes an initial 50 to 60 percent of fluoride. The clarified water is then passed through a bed of activated alumina for further fluoride removal. The activated alumina is regenerated with a 1-percent sodium hydroxide solution, and fluoride in the caustic liquor is effectively precipitated with calcium chloride. The fluoride can be recovered in concentrated form as insoluble calcium fluoride filter cake.

This report was submitted in fulfillment of Grant No. R-804377 by the Feldspar Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period May 10, 1976, to January 31, 1977, and work was completed as of March 22, 1977.

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Mr. Robert E. Anderson, Senior Public Works Operator of the alumina treatment plant in Desert Center, California, was of considerable assistance in his detailed directions pertinent to the regeneration and reactivation of our activated alumina columns.

Keen interest in this project was displayed by the EPA Project Officer, Mrs. Mary K. Stinson, of Edison, New Jersey. Mrs. Stinson gave us detailed instructions for the preparation of this report and helped greatly in keeping the project active to its ultimate conclusion.

# SECTION 1

# INTRODUCTION

## BACKGROUND

Five major and several minor feldspar ore processing plants in the United States use multi-stage flotation methods to separate feldspar from other ore constituents. Hydrofluoric acid is a necessary, key reagent in the feldspar-sand flotation step of the process. Other processes or more environmentally acceptable reagents have proven relatively unsuccessful for a variety of reasons. Some of the plants, including the three operated by the Feldspar Corporation, have made some in-process changes for isolating and reusing flotation water containing hydrofluoric acid. However, a major part of the fluoride introduced during feldspar flotation is eventually diluted and discharged with other plant wastewaters.

The Feldspar Corporation plant at Spruce Pine, North Carolina, as presently operated, produces a combined effluent from the feldspar flotation of 450 to 1,140 liters/min (120 to 300 gpm), with a fluoride content ranging from 60 to 135 ppm. This effluent is combined with other process effluent streams with a flow rate of about 6,430 liters/min (1,700 gpm), containing about 0.25 ppm of fluoride. The combined stream is treated with lime to a pH of 9.5 to 10.0 to flocculate the suspended solids. The lime flocculant does not precipitate a significant amount of fluoride, and the discharge from the plant may contain as much as 23 ppm dissolved fluoride.

Discharge of plant effluents containing large concentrations of fluoride ion into waterways creates a problem because these streams may serve as sources of water for downstream communities and for wildlife. Unless dilution by the water is sufficient (to about 1 ppm or less), the residual fluoride concentration is considered detrimental. Too much fluoride intake by animal life, including man, can result in permanent bone and teeth deformities in the young. At a minimum, fluorosis (mottling of the teeth) can occur and lead to early loss of the teeth. On the other hand, some discharge of fluoride into waterways can be permitted if the background level of fluoride in the water is quite low, and if dilution by the waterway is great. In such areas as Spruce Pine, North Carolina, where there are three wet-process feldspar plants operating, the downstream fluoride levels are closely monitored.

Numerous attempts to remove fluoride from water have generally met with poor to mediocre success. These attempts were based on the use of alum, phosphates, magnesium chemicals, bone char adsorption, and other materials. However, one process presently in use at three known locations in the

United States is successfully and economically removing low concentrations of fluoride from otherwise potable water supplies. This method is based on the adsorption of fluoride on activated alumina.

In the activated alumina process for drinking water, the fluoride-containing water is passed through one or more fixed beds of activated alumina granules, and fluoride adsorbs on the alumina surface. The treated wastewater is then ready for use. Regeneration of fluoride-saturated beds is accomplished by passing dilute sodium hydroxide solution through the beds, followed by washing with dilute acid. Usually two or more fixed beds are used so that the beds can be alternated between adsorption and regeneration cycles.

This process has been used successfully for years in reducing fluorides to the level of 1 mg/liter in potable water supplies. This proven fluoride removal process should be applicable to the feldspar industry problem and also to fluoride-bearing wastewaters of other industries.

Activated alumina is prepared by controlled thermal treatment of granules of hydrated alumina. It is primarily a porous aluminum oxide with a large surface area (a typical grade of activated alumina used for water treatment purposes has a specific surface area of 210 $m^2/g$). The large surface area and the relative polarity of activated alumina make it suitable for adsorptive removal of fluoride from aqueous solution.

The above process for removing fluoride from otherwise potable water is both technically successful and economically feasible. But transferring the application of this simple technology to an equally successful industrial process could require considerable research effort for the following reasons:

- Industrial process wastewaters could contain components that would interfere with fluoride adsorption or alumina regeneration, or otherwise make the process inefficient or uneconomical.

- Because the process wastewater contains large concentrations of fluoride, the activated alumina becomes saturated and requires regeneration very quickly. Since regeneration is the costliest step in the process, frequent regenerations escalate the process cost.

- A lime pretreatment of wastewater will significantly reduce fluoride concentrations and thereby reduce the load on the activated alumina. This step is less expensive than the activated alumina step, but it will require study.

- In the three known plants that produce potable water by activated alumina removal of fluoride, the dilute caustic soda regenerant liquor is simply returned to the environment—i.e., it is dumped on the ground or into river beds that are dry most of the time. This approach cannot be used by industry. High concentrations of fluoride must be recovered and suitably disposed of without hazard to the environment. This need may add a costly step in terms of

additional equipment, chemicals, and manpower.

On April 14, 1976, the Feldspar Corporation in Spruce Pine, North Carolina, was awarded a grant from the Environmental Protection Agency (EPA). The project, which was entitled "Removal of Fluorides from Industrial Wastewaters Using Activated Alumina," was divided into two phases of activity. Phase I provided for the prerequisite laboratory research and development program, plus a preliminary estimate of capital and operating costs for fluoride removal from wastewaters from a typical feldspar wet-process plant. This program was subcontracted to Versar, Inc., in Springfield, Virginia, as this arrangement had been incorporated into the application for the grant. Phase II of the grant provided for the construction of a small pilot plant by Versar, the operation of which was to be conducted primarily by the Feldspar Corporation at their Spruce Pine, North Carolina, plant.

At the completion of Phase I, the Feldspar Corporation concluded that the projected capital cost and the estimated $1.03/kkg ($0.93/ton) of product operating cost placed this method of wastewater treatment outside of the economic scope of the feldspar industry. Consequently, the Feldspar Corporation decided not to pursue Phase II and notified EPA of its decision.

## OBJECTIVES

The objectives of this project were to determine the technical means and the economic feasibility of removing fluoride ion from process wastewaters generated by the feldspar wet-processing industry.

It was realized at an early date that activated alumina could in fact remove small quantities of fluoride (3-10 ppm) from water that was otherwise potable. However, removal of fluoride in concentrations on a larger order of magnitude could prove economically if not technically, infeasible. Therefore, there was little doubt that primary removal of gross amounts of fluoride from water would be required via methods such as precipitation of insoluble calcium fluoride after the addition of calcium hydroxide (slaked lime) or calcium oxide (lime). After this preliminary but gross removal of fluoride, the partially defluoridated water could be subjected to further purification by activated alumina.

Technical and economic optimization of two fluoride-removing techniques were therefore indicated and were the primary objectives of our efforts.

## SECTION 2

## CONCLUSIONS

A multi-stage process has been successfully developed on a laboratory scale to reduce the fluoride ion content of feldspar process wastewater to 5 ppm or less.

The initial fluoride removal step, which consists of treating the feldspar flotation process wastewater with caustic, lime, and calcium chloride and then removing the insoluble calcium fluoride in a clarifier, results in 50 to 60 percent fluoride removal.

On a full plant-scale basis, the process will cost on the order of $1.03/kkg ($0.93/ton) of feldspar product, with an initial capital expenditure on the order of $200,000.

The process is not adversely affected by the presence of most flotation agents, but the activated alumina adsorbent cannot be regenerated if fuel oil is present in the process wastewater.

The undesirable fluoride ion in the process wastewater is recovered as solid, insoluble calcium fluoride. When recovered as a filter cake, calcium fluoride can be sold or stored in regulated landfills.

## SECTION 3

## RECOMMENDATIONS

The process research in this phase has demonstrated the applicability and suitability of removing fluoride from feldspar process wastewater by means of activated alumina. But it has left unanswered the questions pertaining to optimization. Specifically, the areas of concern are:

1. Pretreatment of wastewater with calcium chloride and spent regenerant liquor.

2. Precipitation of fluoride from regenerant liquor with calcium chloride.

3. Recycling of treated process wastewater.

4. Recycling of regenerant.

All four items above are best dealt with on a pilot-plant scale, as they can either be defined much more satisfactorily on a scale larger than the laboratory (items 1 and 2), or they require long-term operations (items 3 and 4) before any effects of recycling streams become apparent.

Consequently, the extension of this project to a pilot-plant scale is recommended, since the proposal is probably applicable to the wastewaters from a number of other industries. Furthermore, the economics will probably not be as onerous to industries that manufacture products with higher unit values than feldspar.

## SECTION 4

## EXPERIMENTAL

A bench-scale test unit was constructed based on two 6-cm (2.5-in) diameter, 76-cm (30-in) high transparent columns containing a bed of activated alumina about 25 cm (10 in) high. In addition, other laboratory equipment such as pumps, valves, tubing, tanks, etc., was purchased as needed. A schematic diagram of the assembled equipment is shown in Figure 1.

For fluoride and pH analyses, an Orion 407A specific ion meter with appropriate electrodes was chosen and purchased. Versar-owned equipment was utilized as required, especially such analytical equipment as a Beckman Acculab IR spectrophotometer and a Heath 704 spectrophotometer.

Process wastewater was shipped from the feldspar plants in Spruce Pine, North Carolina, and Middletown, Connecticut, in plastic-lined, 208-liter (55-gal) drums. Samples of activated alumina were obtained from Kaiser Chemical Corporation, Filtrol Corporation, and Alcoa. Samples of the various reagents utilized in the feldspar flotation process were furnished by Feldspar Corporation. These included frother, oleylamine acetate collector (General Mills "Alamac IIC"), and Williams Company slaked lime.

To evaluate the performance of the activated alumina column, an average (weighted) effluent concentration of 5 ppm of fluoride was selected by Versar and Feldspar Corporation personnel as a practical end point. When the present flow of treated process wastewater (1,140 liters/min or 300 gpm) at a fluoride concentration of 5 ppm is mixed with approximately 6,430 liters/min (1,700 gpm) of other plant effluent (which has a background fluoride level of 0.25 ppm), the total plant effluent should be less than 1 ppm.

Versar personnel made trips to the water treatment plants at Desert Center, California, and Bartlett, Texas, and to the Spruce Pine, North Carolina, plant of Feldspar Corporation. Some detailed data regarding the design and operation of activated alumina treatment plants for potable water supplies were obtained. In addition, better knowledge of a feldspar wet-processing plant resulted for the Versar personnel, and dependable lines of communication were established between Feldspar and Versar. The detailed trip reports appear in Appendix C.

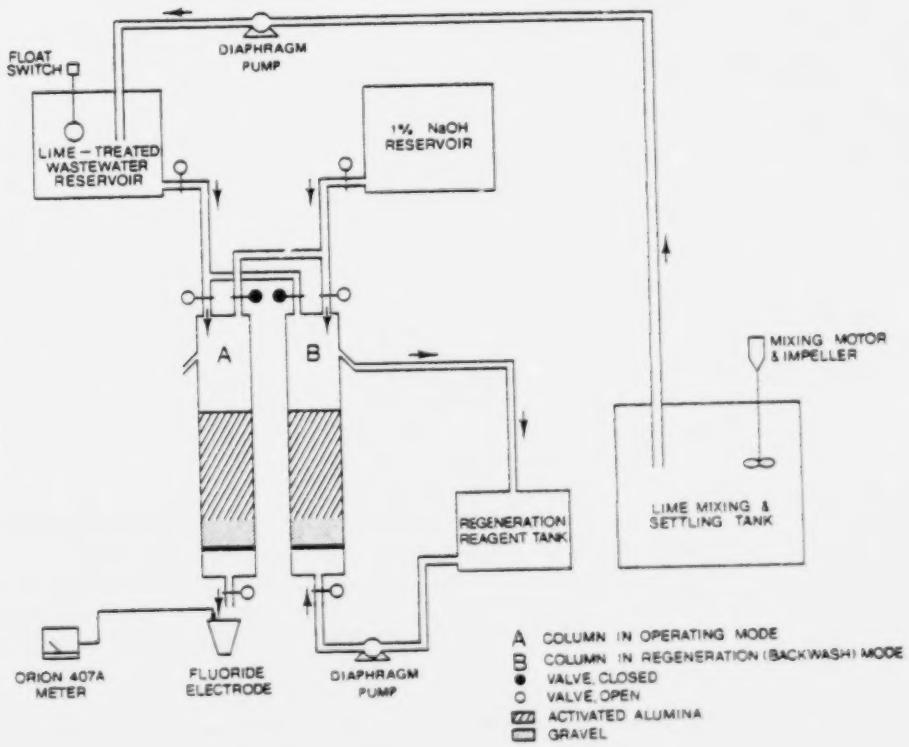


Figure 1. Bench scale system for removal of fluoride from feldspar process wastewater.

## SECTION 5

## RESULTS AND DISCUSSION

### INITIAL TESTS

In the initial test, Spruce Pine process wastewater, at a pH of about 2.5, was neutralized with hydrated lime. This step was necessary because a low pH prevents adsorption of the fluoride by the alumina. After the wastewater was neutralized with lime, a heavy yellow precipitate was formed, and the fluoride content of the wastewater was decreased from 110 to 45 ppm. When the precipitate was isolated by filtration and submitted for analysis, it proved to be roughtly 80 percent calcium fluoride ($CaF_2$) and 20 percent oleylamine acetate (OAA)*, the feldspar flotation reagent.

After removal of the precipitate, the supernatant was pumped to the top of the column of activated alumina and allowed to flow down through the alumina (Alcoa F-1, 28-38 mesh). The run was made with a space velocity of 0.0017 $sec^{-1}$ (residence time of 10 min). It was continued past the initial fluoride breakthrough (81.6 volumes of wastewater per volume of activated alumina) and then past the point at which the average fluoride concentration was 5 ppm (about 120 volumes). The run was arbitrarily halted at 136 volumes, although the alumina was still removing some fluoride.

Regeneration of the alumina was initiated using a 1-percent sodium hydroxide (NaOH) solution as the regenerant. Instrumental analysis of the effluent caustic solution indicated that regeneration was not being accomplished, although regeneration conditions were the same as those established at Desert Center (3 volumes of the above regenerant per volume of media over a period of 20 min).

The above test was repeated, however, without proceeding to saturation of the alumina, and regeneration was again attempted without success.

Two difficulties were recognized as a result of these tests: First, the Orion 407A specific ion meter and fluoride electrode would not detect fluoride ion accurately in the high-pH environment of a 1-percent caustic solution; and second, the activated alumina had co-adsorbed an unknown organic material that could not be removed during caustic regeneration and that prevented regeneration of the alumina. The latter problem proved to be

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* The formula of OAA is:

$$CH_3(CH_2)_7CH = CH(CH_2)_7CH_2NH_3^+,\ CH_3COO^- \qquad MW = 327.6$$

quite difficult, and considerable project time was spent on its eventual solution. The following section discusses these efforts along with a number of other aspects of the process that required study before pilot plant design was feasible. These aspects included removal of fluoride from regenerant, minimum use of caustic in regeneration, process wastewater pretreatment, and acid wash of alumina.

## RESEARCH CONDUCTED

### Detection of Fluoride Ion in a High-pH Environment

The high-pH environment of a 1-percent caustic solution prevented the Orion 407A specific ion meter and fluoride electrode from accurately detecting fluoride ion. This problem was solved by neutralizing such solutions before analysis with a mineral acid that corrected the resulting fluoride analysis by the amount of dilution introduced by neutralization.

### Identification of Organic Co-Adsorbent

Oleylamine acetate (OAA), the feldspar flotation agent, was initially suspected as the adsorbed organic compound, and therefore a study of the extent of OAA adsorption by alumina was initiated. A general analytical method for amines was obtained from the Ashland Oil Co. and was modified slightly to be specific for OAA. This method was used to measure the concentration of OAA in the neutralized and filtered wastewater fed to the alumina column, in wastewater discharged from the column, and in process wastewater received from the feldspar plant.

After considerable effort, it was concluded that OAA was not the alumina co-adsorbent since:

1. Alumina that removed fluoride from synthetic solutions based on fluoride and OAA only was regenerable, and

2. Alumina that removed fluoride from feldspar process wastewater that was several weeks old was not regenerable. This wastewater contained no OAA, since by that time, the compound had completely biodegraded.

A search for other interfering adsorbates was undertaken. In one approach, process wastewater (neutralized and filtered) was contacted with activated charcoal. The charcoal was then washed with freon 113, and this extract was analyzed by infrared spectrophotometry. The most significant peak in this extract was characteristic of a large number of methylene groups. The only compound with this characteristic known to be added to the process at any point was fuel oil. Although the fuel oil was added to the mica flotation step as a flotation agent, this step was followed by two dewatering steps before the feldspar flotation. It therefore appeared unlikely that the fuel oil was passed on in significant quantities.

A visit was made to the Spruce Pine plant where onsite experiments were conducted to identify this contaminant positively and to locate its source. The principal tool used was a Beckman Acculab infrared spectrophotometer.

As a result of this effort, the interfering material was positively identified as fuel oil, and very shortly thereafter, Spruce Pine personnel confirmed that significant quantities of No. 2 fuel oil were added to spar float slurry as a pumping lubricant. Part of the resulting process wastewater stream is recycled to the spar-sand flotation step. This stream contains fuel oil concentrations of 100 ppm or more, depending on the partition of the oil into sand, feldspar, and water from the spar float and from sand overflow.

## Fluoride Removal by Activated Alumina in the Absence of Fuel Oil

A decision on how best to continue the process research work was necessary. Should a process be sought to remove fuel oil, or should the effort concentrate on an oil-free wastewater from another source?

Laboratory experiments showed that activated carbon removed the fuel oil very effectively, but costs for this route were prohibitively high. However, fuel oil addition to process wastewater is not necessarily representative of the entire feldspar wet-processing industry. For example, Feldspar Corporation's plant at Middletown, Connecticut, no longer requires a slurry pump. Their spar float flows by gravity to a vacuum pan filter where a very good spar-water separation is achieved. The decision was therefore made to continue process research on oil-free wastewater. To do this, synthetic solutions and process wastewaters from the Feldspar Corporation's Connecticut plant and from the small Plant #2 at Spruce Pine, North Carolina, were used. These two locations do not use fuel oil as a pumping lubricant, so the use of these plants as a source of process wastewater eliminated problems relating to alumina regeneration.

Connecticut plant wastewater contained about 125 ppm of fluoride and no detectable fuel oil. When it was limed with 0.4 g/liter (0.0033 lb/gal) of calcium hydroxide and allowed to stand for 24 hr, the soluble fluoride content was analyzed at 25.6 ppm. After the calcium fluoride was filtered off, the wastewater was passed through a column of activated alumina. After saturation, the column was regenerated, and two more complete cycles were run with reproducible results. The alumina capacities attained were 5.00, 4.85 and 5.00 kg $F^-/m^3$ (0.312, 0.303 and 0.312 lb $F^-/ft^3$) of alumina at a weighted average effluent concentration of 5 ppm of fluoride. Similar reproducibility was obtained using synthetic fluoride solutions. These results established the feasibility of using activated alumina to remove fluoride from process wastewater that contains no fuel oil.

## Removal of Fluoride from Spent Regenerant

The 1-percent sodium hydroxide solution used for regeneration was essentially unchanged after contacting the alumina, except for a high fluoride content of 500 to 600 ppm or more. Clearly, this solution could not be discharged as waste without reduction of the fluoride level. This step can be accomplished by addition of calcium hydroxide, which precipitates calcium fluoride, as in the pretreatment of the feldspar process wastewater. It was hoped, however, that calcium chloride could be used to accomplish the same purpose at a lower cost.

Accordingly, a number of experiments were carried out to test the efficacy of calcium chloride and to provide some design data. The results are shown in Table 1, where calcium chloride is compared with lime.

Various amounts of calcium chloride and lime were added to spent regenerant liquor. The amount of reagent used was calculated in terms of the ratio of the stoichiometric amount required for formation of calcium fluoride. Spent liquor and reagent were mixed initially and allowed to settle, as was previously done with the liming of process wastewater.

The superiority of calcium chloride over lime is evident and can be attributed to the solubility of the chloride. The low fluoride contents achieved with 10 times the stoichiometric lime requirements probably result from adsorption of fluoride by the insoluble lime, but such quantities are not economically feasible.

Optimal Regeneration of Alumina

During the early phases of this program, process parameters were modeled after those in use at the two drinking water installations visited, and the activated alumina was regenerated with three volumes of 1-percent sodium hydroxide solution per volume of alumina. Attempts were made to decrease caustic soda requirements, because this chemical is the largest single item of cost in the process. Most attempts resulted in incomplete regeneration of the alumina, but a scheme was conceived that accomplishes successful regeneration with one-sixth less caustic. The details of this process step are given in Section 6 of this report. Briefly, the new procedure consists of using all caustic solutions twice. Chronologically, 5.0 volumes of once-used, 1-percent caustic solution are recycled for 30 min through the spent alumina. The stream is then drained off the alumina, and half of it is treated to precipitate fluoride as calcium fluoride. The remaining caustic soda solution is made up to 5.0 volumes by addition of 2.5 volumes of fresh 1-percent solution, which is also recycled continuously through the partially regenerated alumina for 30 min. In the next regeneration cycle, the latter 5.0 volumes of caustic are recycled through the spent alumina.

Further optimization is believed possible using similar techniques. For instance, only 2 volumes of partially spent solution would be discarded from a prior 4-, 5-, or 6-volume caustic batch. By so doing, still another fractional saving of caustic might be possible.

A series of three runs was made using soda ash (i.e., sodium carbonate, $Na_2CO_3$) as a regenerant in lieu of caustic soda. During the third cycle, 55+ volumes of 62 ppm $F^-$ wastewater were passed through the alumina media before the cumulative effluent concentration was 4.8 ppm $F^-$. This corresponds to an alumina capacity of ~3 kg $F^-/m^3$ (~0.2 lb $F^-/ft^3$) alumina. The use of the less expensive soda ash instead of caustic soda is promising, but since the requirement for caustic soda has already been reduced once and further reduction is probable, it would have been fruitless to pursue a new process direction at that time. Moreover, the presence of carbonate might preclude the use of regenerant in neutralizing the process wastewater because of foaming.

TABLE 1. REMOVAL OF FLUORIDE FROM ALUMINA REGENERANT LIQUOR*

| Reagent | Lime [$Ca(OH)_2$] | | | | Calcium Chloride ($CaCl_2$) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Amount used (stoichiometric) | 1.00 | 2.00 | 3.00 | 10.00 | 1.00 | 1.50+ | 2.00 | 3.00 | 10.00 |
| Soluble $F^-$ concentration after 30 min (ppm) | 150 | 140 | 130 | 33 | 84 | 68 | 74 | 66 | 56 |
| Soluble $F^-$ concentration after 1 hr (ppm) | 140 | 130 | 125 | 28 | 68 | 63 | 60 | 56 | 48 |

* A 1-percent NaOH solution containing 560 to 580 ppm $F^-$.

\+ The pH of the regenerant liquor was 12.3; pH after addition of 1.50 times stoichiometric of $CaCl_2$ was 11.8.

## Process Wastewater Pretreatment

Since calcium chloride precipitates fluoride as calcium fluoride in spent regenerant liquor, it should perform equally well in removing fluoride from the process wastewater. The wastewaters are quite acid, however (pH 2.0 to 3.0), and must be neutralized before calcium fluoride would be expected to precipitate rapidly.

Neutralization may be accomplished using the defluoridated, spent regenerant liquor, which is about pH 12 after defluoridation. When process wastewater from the Feldspar Corporation's Connecticut plant (125 ppm $F^-$) was neutralized with spent regenerant liquor (68 ppm $F^-$), the volumetric ratio of wastewater to regenerant was 137:1. The initial pH of the wastewater was 3.8 and that of the regenerant liquor was 11.8. This neutralized wastewater was treated further by the addition of powdered calcium chloride for a calcium/fluoride equivalence of 4/1. The resulting pH of the solution was 6.7, and there was little or no precipitation of calcium fluoride at that point. However, when the pH was adjusted to 7.3 using less than 0.1 slaked lime [$Ca(OH)_2$] per liter of solution, the fluoride was precipitated as calcium fluoride.

Additional experiments with calcium chloride and lime showed similar results. Fluoride does not precipitate appreciably until the solution is made alkaline, but one can conclude that calcium chloride is more effective than lime as the precipitant because of its greater solubility. Also, the nature (composition as related to source, age, etc.) of the process wastewater appears to have some effect on the efficacy of fluoride precipitation.

To obtain design data for pretreatment, a "worst case" was studied in which lime alone was used to remove the fluoride and neutralize the wastewater (the limited solubility of the lime would give the lowest rate of fluoride precipitation and therefore the largest size for a clarifier or settling tank). Connecticut plant wastewater was limed in the laboratory at room temperature using 0.4 g/liter (0.0033 lb/gal) calcium hydroxide [$Ca(OH)_2$]. Two cases were studied: one with agitation and the other without agitation except for initial mixing. Fluoride ion was monitored with the Orion 407A apparatus.

As shown in Figure 2, reduction of fluoride was rapid initially, but was not complete for 6 to 8 hr. About 50 percent, or slightly more, of the fluoride was precipitated during the first 30 min. Surprisingly, the unagitated case appears superior to the continuously agitated case.

Optimization of the use of spent regenerant in combination with calcium chloride would be better studied in a pilot plant environment where rate studies can be made as a function of residence time and where age of the process wastewater is more nearly representative of actual conditions.

## Acid Washing of Activated Alumina

A number of acid washing techniques were used for neutralizing the activated alumina after caustic regeneration. These included the use of

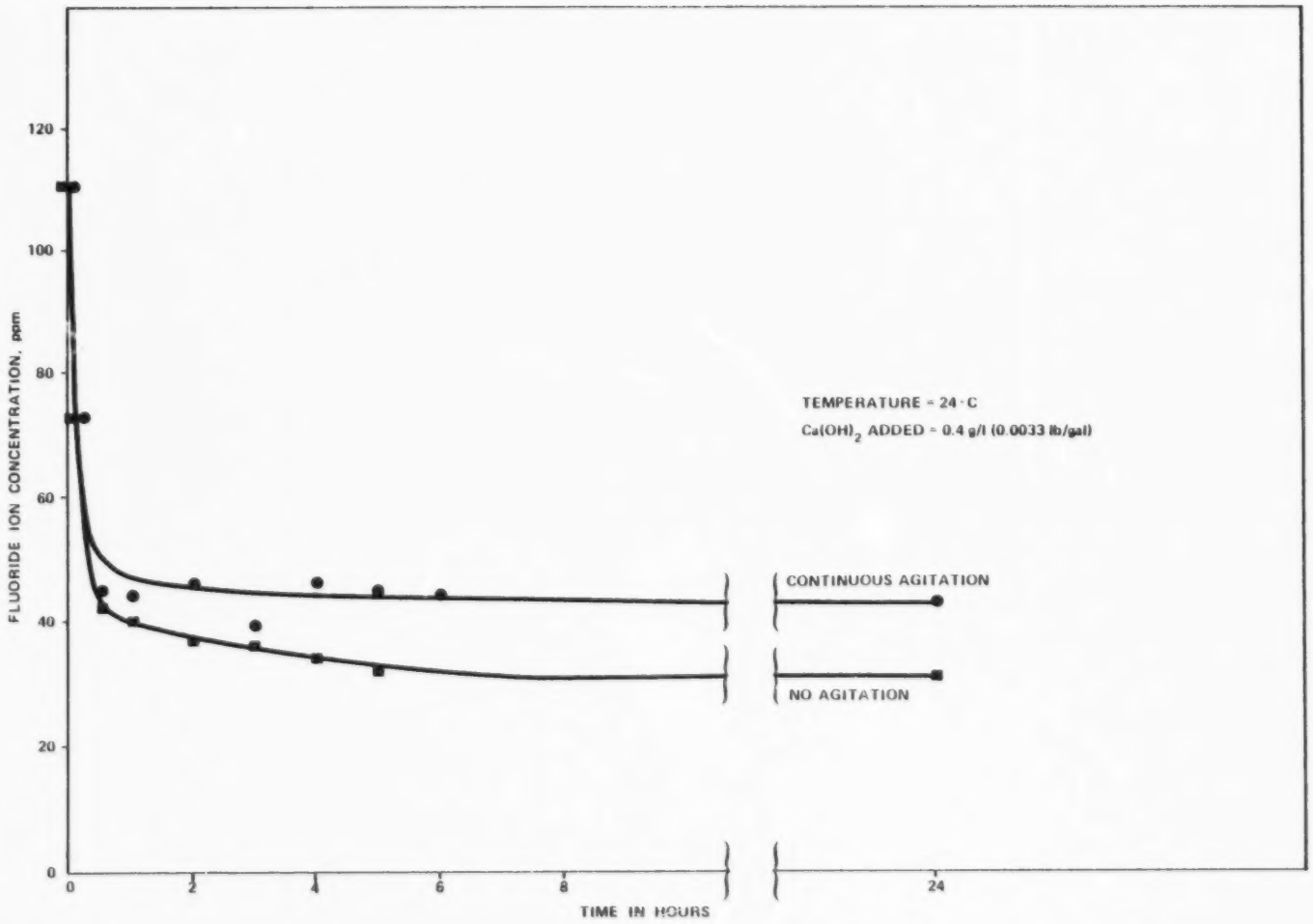


Figure 2. Partial removal of fluoride from feldspar process wastewater by calcium hydroxide.

hydrochloric acid and sulfuric acid solutions up to 2 percent. Neither was technically superior to the other, so dilute sulfuric acid was selected because:

- It is cheaper,
- In concentrated form, it can be handled in carbon steel equipment, and
- Feldspar plants generally use sulfuric acid in other steps and already have acid storage facilities.

Washing time and wash water velocity appear to be more important than acid strength in neutralizing the beds. Accordingly, the following procedure is recommended: backwash regenerated activated alumina for no less than 45 min using wash water maintained at pH 6.8 (+0; -0.4), at a space velocity of 0.00417 $sec^{-1}$ (4 min residence time). Washing cycles in excess of 45 min can do no harm. Wash water can be made up by diluting 5 volumes of neutral water with 1 volume of 1-percent sulfuric acid.

## Activated Alumina Testing

Initial experimental work using activated alumina was based on the Alcoa F-1 product (28-38 mesh), since this was the alumina used at the Desert Center, California, and Bartlett, Texas, installations. Two other commercially available activated alumina products were obtained from the Filtrol Corporation, Jackson, Mississippi and from the Kaiser Aluminum and Chemical Corporation, Baton Rouge, Louisiana. Both products were screened for use in this process but proved inferior to the Alcoa product. No further effort was expended in this direction.

## SECTION 6

## SUMMARY OF PROCESS FOR REMOVING FLUORIDE FROM FELDSPAR PROCESS WASTEWATER

1. Process wastewater at pH 2.0 to 3.0 is treated with three chemicals--lime, calcium chloride and a once-used alumina regenerant (1-percent sodium hydroxide solution in an in-line mixer). The result is an increase in pH to about 7.3 and formation of calcium fluoride precipitate.

2. Calcium fluoride ($CaF_2$) settles out as a slurry at the bottom of a settling tank. Residence time in the tank is a minimum of 30 to 35 min and preferably 1 hr. Periodically calcium fluoride slurry is pumped from the bottom of the tank to a filter.

3. Settling tank overflow passes through a column of activated alumina and then leaves the plant, proceeding either to the river or to mixing with other effluents. This water can also be recycled in the feldspar processing plant, as it is of good quality.

4. While one of the two columns of activated alumina is processing wastewater, the other is being regenerated. About 48 volumes of pretreated wastewater at 60 ppm fluoride will saturate 1 volume of activated alumina.

5. When being regenerated, a column of activated alumina is first backwashed with 5 volumes of previously used 1-percent sodium hydroxide (NaOH) solution per volume of activated alumina for 30 min with a space velocity of 0.00417 $sec^{-1}$ (residence time of 4.0 min).

6. Then 2.5 volumes of the used sodium hydroxide solution are pumped to a settling tank where they are mixed with 1.5 moles of calcium chloride (in aqueous solution) per mole of fluoride ($F^-$). After the calcium fluoride has settled out, the clear supernatant sodium hydroxide solution is used either to neutralize incoming fluoride-containing process wastewater (see step 1) or to neutralize other non-fluoride plant effluents before discharge. Calcium fluoride slurries from the bottom of the settling tank or clarifier are pumped to the same filter as in step 2 for concentration of the calcium fluoride precipitate. The recovered calcium fluoride is either sold and shipped, or stored in a secured landfill.

7. The column of activated alumina is then further backwashed with 5 volumes of 1-percent sodium hydroxide solution for 30 min with a space velocity of 0.00417 $sec^{-1}$ (4.0 min residence time). Half of this solution was left over from the prior regeneration cycle, and half is fresh make-up solution. After this backwashing, the entire 5 volumes of partially spent hydroxide solution are drained off the alumina and retained; 2.5 volumes of it

are used in the initial regeneration step of the next cycle (step 5).

8. Regeneration is completed by continuously backwashing the alumina for 45 min or more with 5 or more volumes of wash water maintained at a pH of 6.8 (+0; -0.4), again with a space velocity of 0.00417 $sec^{-1}$. Washing cycles of less than 45 min will result in decreased alumina capacity for fluoride; cycles in excess of 45 min do no harm. Approximately half of the used acid wash water should be discharged as plant effluent after each regeneration cycle. Make-up wash water is obtained by acidulating river water (approximately 5 volumes of water plus 1 volume of 1-percent sulfuric acid).

A flowsheet for the feldspar wastewater defluoridation process is given in Figure 3.

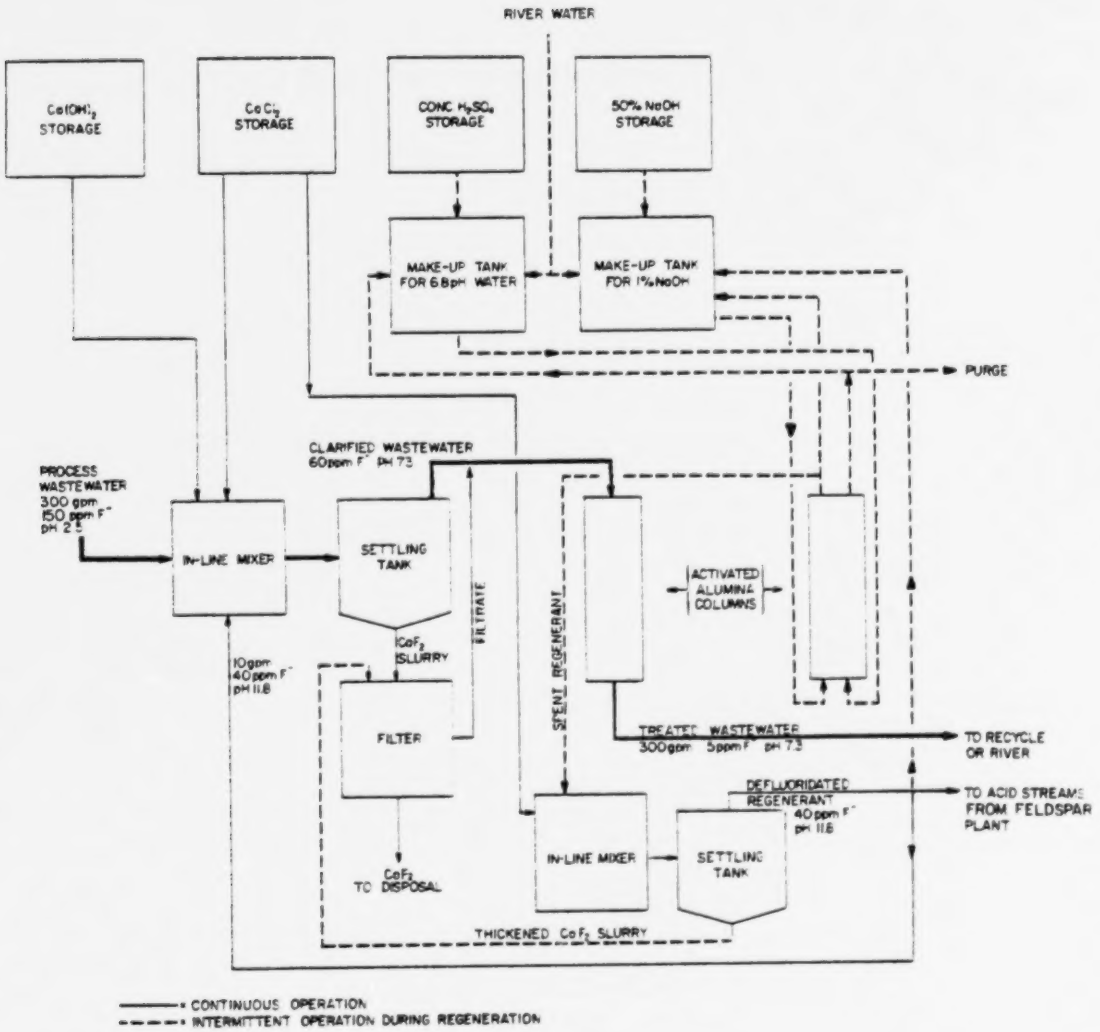


Figure 3. Feldspar wastewater defluoridation process flow diagram.

## SECTION 7

## ECONOMICS

An economic evaluation has been prepared for the feldspar wastewater defluoridation process. Capital and operating costs for the proposed process are summarized in Table 2, and equipment costs are shown in Table 3.

For a 163,000 kkg/year (180,000 ton/year) plant, the initial capital expenditure was estimated to be about $200,000. The projected unit cost for removing at least 92 percent of the soluble fluoride from feldspar flotation process wastewaters using the four-step process outlined here is $1.03/kkg ($0.93/ton).

Some reductions in operating costs appear possible with process optimization, particularly those associated with the caustic regeneration of activated alumina. Other possible economies include:

--Substitution of calcium chloride for the more expensive lime in the initial treatment of process wastewater;

—Partial recycling of spent regenerant liquor during alumina regeneration to conserve sodium hydroxide;

—Recycling of once-used regenerant liquor to neutralize incoming low-pH feldspar process wastewater; and

--Use of excess treated alumina regenerant liquor (sodium hydroxide solution) as partial or whole replacement of presently used lime for pH adjustment of the total plant effluent.

Cost reductions that could result from these steps have not been calculated, nor have those that might accrue from the sale of the calcium fluoride cake.

TABLE 2. ECONOMICS SUMMARY

| Item | | Cost | Cost/kkg feldspar * (Cost/ton feldspar) |
|---|---|---|---|
| Estimated initial capital expenditure for fluoride removal from process wastewater | | $200,000 | -- |
| Estimated annual operating costs for fluoride removal: | | | |
| [Capital recovery], 10% interest rate, 10-year depreciation | | 33,400 | $0.2046 (0.1856) |
| Maintenance, 6% of capital/year | | 12,000 | 0.0735 (0.0667) |
| Taxes and insurance, 2% of capital | | 4,000 | 0.0245 (0.0222) |
| Power, 46 hp @ 2.2¢/kwh | | 5,700 | 0.0346 (0.0314) |
| Labor, 1 operator/shift, $300/week each including supervision, overhead, etc. | | 47,000 | 0.2867 (0.2600) |
| Chemicals: | | | |
| Activated alumina | $0.4010/kkg ($0.3637/ton) | 65,000 | 0.0252 (0.0229) |
| Lime | | | 0.0198 (0.0180) |
| Caustic soda | | | 0.2862 (0.2596) |
| Sulfuric acid | | | 0.0119 (0.0108) |
| Calcium chloride | | | 0.0578 (0.0524) |
| | | | ~$1.03 (~$0.93) |
| Total | | $168,000 | |

* Based on a production rate of 163,000 kkg/year (180,000 ton/year) of feldspar.

TABLE 3. ESTIMATED COSTS FOR MAJOR EQUIPMENT ITEMS

| Number required | Description | Estimated cost installed |
|---|---|---|
| 1 | In-line mixer or mixing tank (agitated), 1,000-gal | $ 9,000 |
| 1 | P.W.W. settling tank, slanted bottom w/bottom slurry discharge, 10,500-gal | 16,500 |
| 2 | Columns, activated alumina 125 $ft^3$ media | 48,400 |
| 1 | Filter, vacuum, disc | 14,600 |
| 1 | Tank, storage, 50% NaOH, 4,000-gal | 8,200 |
| 1 | Tank, recirculation, 1% NaOH, 5,000-gal | 10,000 |
| 1 | Tank, recirculation, 6.8% pH, 5,000-gal | 10,000 |
| 1 | Tank, storage, 40% $CaCl_2$, 11,000-gal | 17,000 |
| 1 | Tank, settling, 1% NaOH, 6,000-gal w/bottom outlet | 11,200 |
| 5 | Pumps, 300-gpm | 6,600 |
| 1 | Feeder, dry lime | 3,000 |
| 2 | Pumps, 10-gpm | 2,300 |
| 2 | Pumps, 5-gpm | 2,300 |
| | Total | $159,000 |

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# APPENDIX A. SUMMARY OF EXPERIMENTAL TESTS ON ALCOA ACTIVATED ALUMINA

TABLE A-1. SUMMARY OF RUNS ON ALCOA ACTIVATED ALUMINA

| Run No. | Initial $H_2O$ wash | | | Caustic Treatment | | | | Caustic Neutralization | | | | Final $H_2O$ rinse | | | Stream | Residence Time (min) | Vol. W/W Vol. $A_2O_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Amount | Mode | Time (min) | Amount (liters) | Concentration, NaOH | Mode | Time (min) | Amount (liters) | Concentration | Mode | Time (min) | Amount | Mode | Time (min) | | | |
| 1 | | | | 3 | 2% | ST | | 3 | 1.5% HCl | RF | 30 | 1 liter | ST | | S.P. | 2 | 17.4 |
| 2 | | | | 3 | 2% | ST | | 3 | 1.5% HCl | RF | 30 | 1 liter | ST | | S.P. | 2 | 20 |
| 3 | | | | 3 | 2% | ST | | 3 | 1.5% HCl | RF | 30 | 1 liter | ST | | S.P. | 4 | 48.5 |
| 4 | x 5 | RR | 30 | 3 | 2% | ST | | 3 | 1.5% HCl | RF | 30 | 1 liter | ST | | S.P. | 4 | 0 |
| 5 | x 5 | RR | 30 | 2 | 2% | ST | | 2 | 1% HCl | RR | 10 | x 5 | RR | 15 | S.P. | 4 | 0 |
| 6 | | | | 4 | 1% | RR | 10 | 2 | 1% HCl | RR | 10 | x 5 | RR | 15 | S.P. | 4 | 17.5 |
| 7 | x 5 | RR | 15 | 3 | 2% | ST | | 1 | 1% HCl | ST | | x 5 | RR | 15 | S.P. | 4 | 12.2 |
| 8 | x 5 | RR | 15 | 8 | 2% | ST | | 1 | 1% HCl | ST | | x 5 | RR | 15 | S.P. | 4 | 0 |
| 9 | x 5 | RR | 10 | 4 | 2% | RR | 10 | 3 | 1% HCl | RR | 10 | x 5 | RR | 10 | S.P. | 4 | 8.7 |
| 10 | x 5 | RR | 30 | 8 | 1% | ST | | 8 | pH 2.5 $H_2SO_4$ | RR | 15 | x 5 | RR | 15 | S.P. | 4 | 0 |
| 11 | x 5 | RR | 30 | 8 | 1% | ST | | 12 | pH 2.5 | RR | 40 | | | | S.P. | 4 | 0 |
| 12 | x 5 | RR | 30 | 6 | 1% | ST | | 28 | 1% $H_2SO_4$ | ST | | x 5 | RR | 15 | S.P. | 4 | 0 |
| 13 | | | | 3 | 1% | ST | | 3 | 1% $H_2SO_4$ | RR | 30 | | | | S.P. | 4 | 0 |
| 14 | x 5 | RR | 30 | 3 | 1% | RF | 30 | 5 | 1% $H_2SO_4$ | RR | 30 | x 5 | RR | 30 | S.P. | 4 | 27.5 |
| 15 | x 5 | RR | 30 | 3 | 1% | RF | 30 | 5 | 1% $H_2SO_4$ | RR | 90 | x 5 | RR | 30 | S.P. | 4 | 0 |
| 16 | | | | 5 | 1% | RR | 30 | 5 | 1% $H_2SO_4$ | RR | 90 | | | | Syn. | 4 | 0 |
| 17 | | | | 4 | 1% | RR | 30 | 4 | 6.8 pH | RR | 60 | 2 liters | RR | 15 | Syn. | 4 | 0 |
| 18 | | | | 4 | 1% | RR | 60 | 4 | 6.8 pH | RR | 30 | 2 liters | RR | 30 | Syn. | 4 | 0 |
| 19 | | | | 4 | 1% | RR | 60 | 4 | 6.8 pH | RR | 60 | 2 liters | RR | 30 | Syn. | 4 | 0 |
| 20 | | | | 4 | 1% | RR | 60 | 4 | 6.8 pH | RR | 90 | 2 liters | RR | 30 | Syn. | 4 | 0 |
| 21 | | | | 4 | 1% | ST | | 5 | 6.8 pH | RR | 60 | 2 liters | RR | 30 | Syn. | 4 | 45 |
| 22 | | | | | | | | 4 | 6.0 pH | RR | 60 | | | | Syn. | 4 | 32.5 |
| 23 | | | | 2 | 1% | RR | 30 | 4 | 0.2% $H_2SO_4$ | RR | 15 | | | | Syn. | 4 | 43.7 |
| 24 | | | | 4 | 1% | RR | 30 | 4 | 0.2% $H_2SO_4$ | RR | 45 | | | | Syn. | 4 | 60 |
| 25 | | | | | | | | 4 | 0.2% $H_2SO_4$ | RR | 15 | | | | Syn. | 4 | 50 |
| 26 | | | | | | | | 4 | 0.2% $H_2SO_4$ | RR | 15 | | | | S.P. | 4 | 58.7 |
| 27 | | | | | | | | 4 | 0.2% $H_2SO_4$ | RR | 15 | | | | S.P. | 4 | 58.7 |

Run Nos. 1 - 15, with fuel oil
Run Nos. 26 and 27, without fuel oil
Symbol
RR = recycled in reverse direction (backwash)
RF = recycled in forward direction
ST = straight through (no recycling)
Bed volume in all cases = 0.805 liters

## APPENDIX B. ANALYTICAL METHODS

### Determination of Fluoride Concentration in Aqueous Solutions

**Application:** This direct readout method for fluoride determination was followed so that activated-alumina-treated waters could be analyzed for fluoride concentration rapidly.

**Principle:** Direct readout of fluoride as free species is possible using the logarithmic scale of an Orion 407A meter after the scale has been calibrated with known standards.

**Apparatus:** Orion 407A meter
Fluoride-specific electrode

**Reagents:** Total ionic strength adjustment buffer (TISAB)

**Procedure:** Make fluoride standards of 1, 10, and 100 ppm and dilute 1:1 with TISAB. Place electrode in 10-ppm standard and turn calibration control to get a center-scale reading.

Rinse electrodes, blot dry and place in the 100-ppm standard. Turn the temperature compensator until needle points to right-hand full scale line.

Rinse electrodes, blot dry, place in unknown solution that has been diluted 1:1 with TISAB. Multiply the reading on the logarithmic scale by the center-scale value to determine the unknown concentration.

**Note:** With the various standards, it is possible to set center scale at 1, 10, or 100 ppm, depending on the fluoride concentration range of unknowns.

### Determination of Fluoride Concentration of Highly Alkaline Streams Containing Aluminum Ions ($Al^{+++}$)

**Application:** Regenerant streams, typically 1% NaOH, were found to contain ~360 ppm aluminum. $Al^{+++}$ interferes with accurate fluoride readings obtained using fluoride-specific electrode.

**Principle:** TISAB contains 4 g/liter 1,2-cyclo-dinitrilo tetra-acetic acid (CDTA), which preferentially chelates small amounts of $Al^{+++}$. By increasing CDTA to ~45 g/liter in TISAB, the $Al^{+++}$ interference limit is increased to 38 ppm.

**Apparatus:** Orion 407 meter
Fluoride-specific electrode

**Reagents:** Modified TISAB (modified in-house)

Procedure: Dilute samples 1:10 with distilled water, and again 1:1 with modified TISAB. Compare millivolt reading from expanded millivolt scale to standard curve obtained by the same method.

## Infrared Spectroscopic Analysis of Freon Extracts of Process Wastewater

Application: One or more of the organic flotation reagents routinely used in the Spruce Pine facility, or an unsuspected organic material, was blinding the activated alumina and preventing alumina regeneration.

Principle: A great many organic compounds have characteristic infrared spectroscopic profiles, and such profiles can be used to identify organics.

Apparatus: Separatory funnels, 125-ml
Beckman Acculab IR
Two matched adsorption cells, 1-cm, quartz
1- x 30-cm glass columns (alumina)
1- x 30-cm glass columns (activated carbon)

Reagents: Freon 113

Procedure: To a 125-ml separatory funnel, add 10 ml of sample and 10 ml of Freon 113. Shake well and let stand for 10 min. (Ratio of 10 ml sample/10 ml Freon may be insufficient if organic concentration is too minute). Drain off Freon layer into one of the matched cells. Fill the other (reference) cell with Freon. Place reference cell and sample cell in respective positions in the Acculab. Scan from 2.5 microns (4,000 $cm^{-1}$), to 5 microns (2,000 $cm^{-1}$).

| Run No. | Compounds or Materials Tested |
|---|---|
| 1 | Polypropylene glycol |
| 2 | Sulfonated white oil |
| 3 | Alcohol type frother |
| 4 | No. 4 fuel oil |
| 5 | Tap water |
| 6 | Freon extract of process wastewater |
| 7 | Freon extract of process wastewater after lime treatment (pH adjustment) |
| 8 | (a) Freon extract of unused activated carbon (Filtrasorb 400)<br>(b) Freon passed through activated carbon (Filtrasorb 400) after process wastewater |
| 9 | Freon passed through activated carbon after process wastewater |
| 10 | (a) Process wastewater extracted with Freon after passage through activated alumina<br>(b) Freon passed through activated alumina after process wastewater |
| 11 | Freon passed through alumina after process wastewater |

Determination of Trace Amounts of Amines in Aqueous Solutions

Application: This method can be used to determine trace amounts of amine in aqueous solutions to a level as low as 0.5 ppm.

Outline: The amine complexes with methyl orange to form a yellow solution which is extracted into chloroform and measured in the visible range on a spectrophotometer at 420 mu. The amount of amine in the sample is determined by comparing it with stand ards run by the same method.

Specifications and Directions:

A. Apparatus
   1. Separatory funnels, 250-ml
   2. Beckman DK-2 spectrophotometer or equivalent
   3. Two matched absorption cells, 1-cm, quartz

B. Reagents
   1. Methyl orange - acid buffer reagent. Dissolve 0.1 g of methyl orange in distilled water. Dissolve 29.6 g of sodium acetate trihydrate and 50 g of potassium chloride in water. Combine the two solutions, add 100 ml of glacial acetic acid, and dilute to 500 ml with water
   2. Chloroform AR
   3. Isopropyl alcohol AR
   4. 1 percent NaOH solution.

C. Procedure

Titrate test solution with 1 percent NaOH to a pH of 7.0. Note amount of NaOH required for computation of dilution factor. (This step will negate the possible effect of the HF acidity of the solution on the indicator.)

To a 250-ml separatory funnel, add 500 ml of the sample to be tested. Add 5 ml of the methyl orange reagent, shake, and set aside for 10 min. Add 20 ml of chloroform and shake for 5 min.

Allow to separate for 3 min. Drain off the chloroform layer, add 0.5 ml of isopropanol, and measure absorbance (A) immediately on a spectrophotometer at 420 mu. It is important to be consistent in the timing because the color is very unstable.

NOTE: If necessary, dilute extracted layer with chloroform before reading.

Make standard solutions of the amine to be measured (1.0, 3.0, 5.0 and 7.0 ppm of amine). Run these by the above procedure and plot a standard curve of the absorbances (A). The ppm of amine in the unknown can be read from the curve and multiplied by the dilution factor.

APPENDIX C. TRIP REPORTS

TO: R. Shaver, R. Smith, E. Juergens
File, Feldspar Corp. (2 copies)

FROM: I. Frankel

Date: 8 June 1976

Subject: Trip Report, Visit to Alumina Treatment Plant, Riverside County Service Area 51, Desert Center, California 92239

5-27-76

Contact: Mr. Robert E. Anderson
Sr. Public Works Operator
Phone: (714) 227-3203

The writer was with Mr. Anderson during a 4- to 5-hr period during which the operation and equipment of the alumina treatment plant was discussed. The plant itself was inspected, as was the sewage treatment system. Mr. Anderson had prepared a two-page process description in advance of my visit, and this provided an excellent basis for our further discussion. This material is reproduced in Figure C-1.

Desert Center is a small southern California community on Interstate 10, about 89 km (55 mi) west of Arizona. The area is desert and sparsely populated. The community is divided into two parts: A business district with stores, restaurants, and service stations at the exit from I-10, and a pleasant residential area about 2.4 km (1.5 mi) north of the highway. The latter is irrigated and therefore is grassy with some trees. A few farms nearby grow dates and citrus fruit by means of irrigation.

The residential area was planned and financed by the Kaiser Steel Co. to accommodate mine supervisory and management personnel and their families. The nearby Iron Mountain mine is a large source of iron ore from Kaiser's western steel operations. Water for the community is obtained from deep wells and is of potable quality except for fluoride content.

The incoming well water has a fluoride content of 7.5 ppm, which is reduced to 0.8-1.2 ppm in the subject plant. The lower fluoride value is obtained in the summer, and the higher value in winter. Thus the human intake is adjusted to an average year-round value of 1.0 ppm.

Fluoride removal is accomplished by passing the well water through a bed of activated alumina (media). During the period before the need for media regeneration, the $F^-$ concentration in output water is as low as 0.2 to 0.3 ppm. However, as indicated above, the average value of distributed water is maintained at 0.8 to 1.2 ppm. In 7 years of operation there has been no requirement for replacement of media. Media addition to the extent of 15 to 20 percent has taken place twice during that period.

Operation of the defluoridation system is simple and consists of four cycles, as follows:

(a) Gravity flow of pH adjusted water (5.0-6.0) through one or both parallel media tanks. Flow can be continuous, or part time, depending on the water level in the reservoir.

(b) When the media in tank begin to indicate breakthrough (by an increasing level of $F^-$ in the product water), the water flow is reversed and the media bed is expanded (to approximately 200 percent of its settled volume). After washing out silt and iron oxide, the bed is aerated for a bit less than 5 minutes. The aeration tends to enhance or help sustain media activity toward $F^-$ ion removal.

(c) Regeneration is accomplished by downflow of caustic solution during a period of 30 minutes.

(d) The bed is then neutralized by gravity feeding of low pH (2.5-3.0) water. Excess exposure to acid waters, or excess acidity should be avoided, else the media itself will become acidic and will not remove fluoride without a reverse neutralization. Specific operating and performance data for the above steps are given on sheets attached to this report.

At Desert Center, the media tanks are constructed of steel, and the acid storage tank is made of fiberglass-lined steel tanks. Underground piping is concrete-lined steel. None of these materials would be recommended for these applications in a new system. The media tanks should be fiberglass-lined steel, the acid tanks should be carbon steel, and no concrete-lined pipes should be used.

Fluoride content of treated and untreated water is determined with a Hach DR/2 spectrophotometer. A water sample is mixed with a reagent, placed in a glass cell, inserted into the unit, and the $F^-$-ion concentration is read directly. Any given analysis takes only a minute or less. When originally constructed, this plant was highly instrumented and automated, and a Beckman Model 900 fluoride ion analyzer was purchased for process control. This instrument was probably one-of-a-kind, and it was not accurate. It was never used except during the start-up tests. Other initial installed automation devices were also discarded, modified, or brought into use over a period of years, as opposed to the initial design mode.

Other water quality analyses are performed by Mr. Anderson or his assistant, as needed. A copy of their operating log sheet is attached. Furthermore, county health officials check water quality once per month and arrive unannounced to sample onsite.

Another $F^-$-ion removal plant was built in 1973 in a suburban Tucson, Arizona, development. Its capacity is about 25 percent of the Desert Center unit, but its design was based on and benefited by the experiences of the Desert Center operation, particularly with respect to materials of construction. It is alleged to be operating satisfactorily, and it also uses Alcoa F-1, 28 to 48 mesh media.

Present costs for fluoride removal at Desert Center are 5¢/1,000 liters (19¢/1,000 gal). The costs include labor, chemicals, and power, but no depreciation. A breakdown of this cost will be provided by Mr. Anderson in the near future. Labor application is approximately equivalent to one-third of a man-day. Only two men are used for operation and maintenance of the deep wells, the fluoride removal plant, the sewage plant, and the water distribution and sewage collection systems. Heavy maintenance is performed by outside contractors.

Figures C-2, C-3 and C-4 show, respectively, a schematic flowsheet of the Desert Center defluoridation plant, a crude sketch of the construction of a media tank, and a sketch of the plastic spargers mounted on the steel plate on the bottom of the media bed. These spargers were purchased from the Eimco Corporation, Salt Lake City, and they are quite effective in allowing defluoridated water to be collected without loss of media and in permitting good backwashing and aeration during the initial stages of media cleanup and regeneration.

Desert Center, California, Operating and Design Parameters

1. Defluoridation

   a. Two tanks in parallel flow, used sequentially or at the same time.
   b. 17 $m^3$ (600 $ft^3$) media (activated alumina) in each tank.
   c. Each 0.028 $m^3$ ($ft^3$) of media will treat about 16,000 liters (4,200 gal) of water at a rate of ~134 liters/$m^3$ min (~1 gal/$ft^3$-min). Removal of $F^-$ is 3,999 g/$m^3$ (1,700 g/$ft^3$) (maximum of 130 g (2,000 gr), which is equivalent to 3.9 kg $F^-$/$m^3$ (0.243 lb $F^-$/$ft^3$).
   d. Media is 24 to 48 mesh Alcoa F-1 activated alumina.
   e. Incoming water is pretreated to 5.0 to 6.0 pH with controlled input of sulfuric acid.
   f. Defluoridation is not continuous; the system is operated in line with water demand and reservoir level.
   g. Other than pH control, incoming well water is not pretreated. After defluoridation, the only post-treatment of the water is the use of NaOH to bring the pH to ~7.0.

2. Backwashing and Aeration

   a. Start backwashing at 1,900 liters per min (500 gpm). Increase to 3,800 liters per min (1,000 gpm) for several minutes. Decrease the rate to 1,900 liters per min (500 gpm) and aerate for ~5 min.
   b. Total backwashing water is 76 to 114 $m^3$ (20,000 to 30,000 gal).

3. Regeneration

   a. Regenerating fluid is a 1-percent solution of caustic soda (NaOH).
   b. Use 3 bed volumes ( 5 $m^3$ or 1,800 $ft^3$) of regenerant over a period of 30 min (S.V. = 0.00167 $sec^{-1}$, or residence time of 10 min).

LAKE TAMARISK DEFLOURIDATION PLANT
RIVERSIDE COUNTY SERVICE AREA #51
DESERT CENTER, CALIF.

TANK #_____

RUN #_____ OPERATING LOG DATE _____

PRE-REGENERATE RINSE TO LAND

Meter-end =_____
Meter-start =_____
Total Gals. $H^2O$=_____

REGENERATE SOLUTION

Meter-end =_____
Meter-start =_____
Volume Caustic
(50% NaOH) =_____

NEUTRALIZATION RINSE TO PONDS

Time-end =_____
Time-start =_____
Total Min.___x ___ gpm = ___ GAL.

NEUTRALIZATION RINSE TO LAND

Time-end =_____
Time-start=_____ Fluoride Av.____
Total Min.___x ___gpm = _____ GAL.

TOTAL WASTEWATER SUMMARY

Total Land_____ Gals.
Total Ponds_____ Gals.
Total Waste_____ Gals.

SERVICE TO RESEVOIR

Meter-end _____
Meter-start_____
Quantity Treated_____ Gals.

Total Water used _____Gals. Percent Waste _____%

TREATED WATER PROGRESSIVE LOG

| DATE | meter reading | (A) 1000 Gals. treated | (B) cumulate column (A) | (C) fluoride reading | (D) average fluoride | (E) column (A)x(D) | (F) column (E) | (G) aver. fluoride (F)x(B) | oper. |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | |

Figure C-1. Process description.

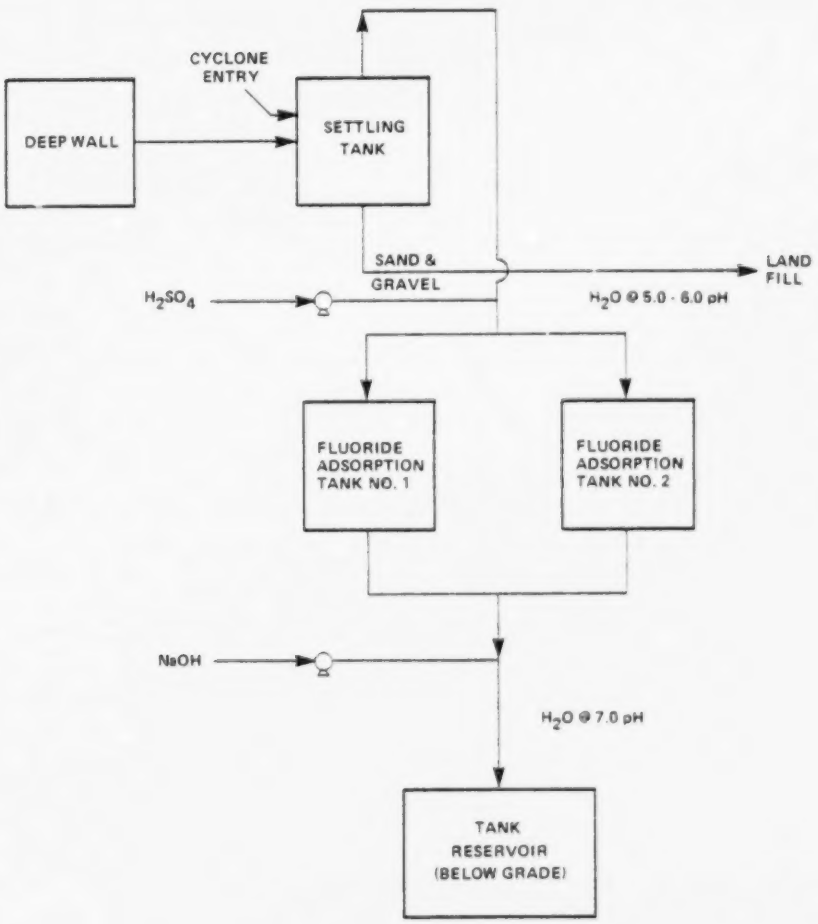


Figure C-2. Schematic flow plan for defluoridation of Desert Center California, Potable water.

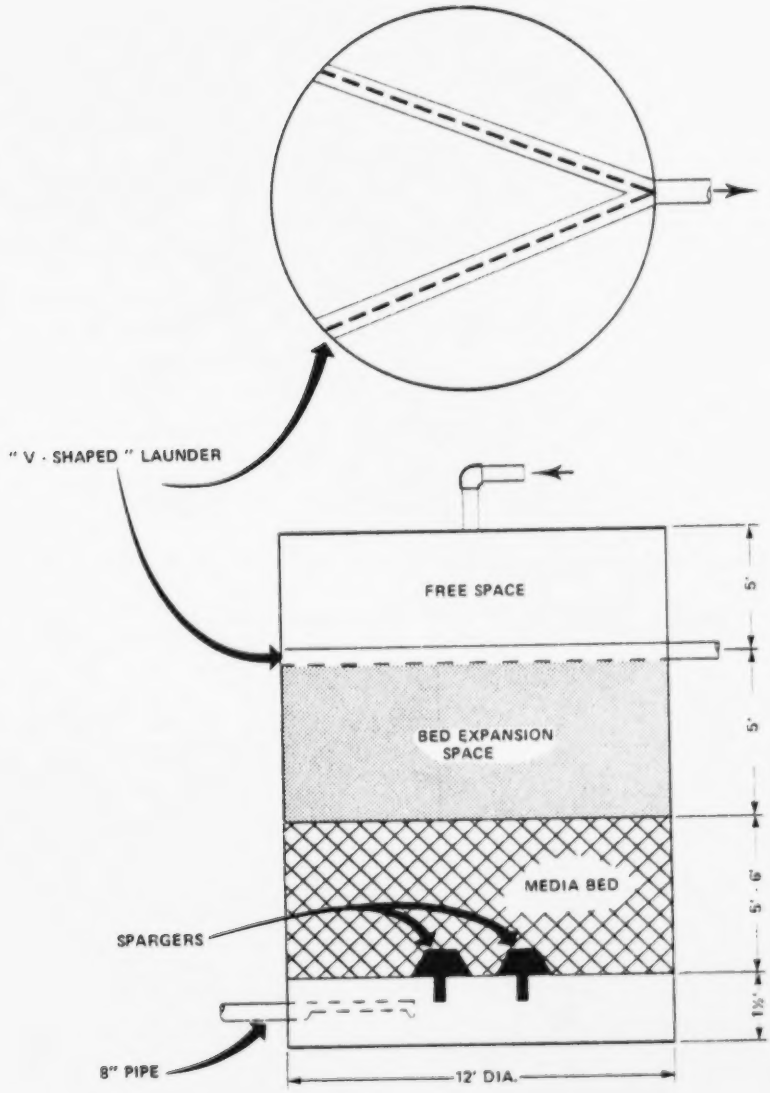


Figure C-3. Sketch of media tank design.

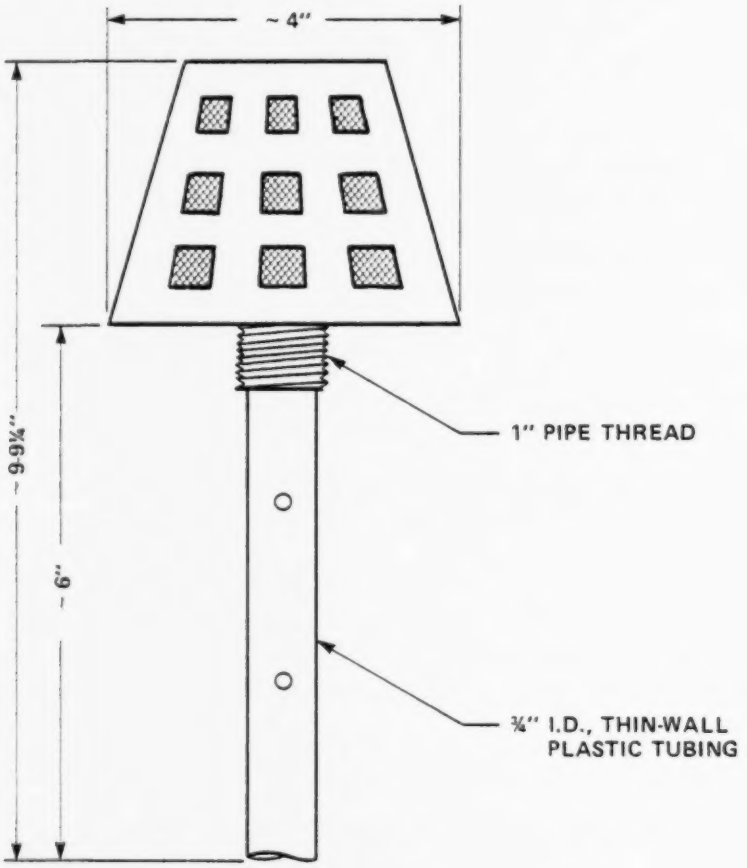


Figure C-4. ELMCO plastic sparger (probably nylon).

LAKE TAMARISK DEFLUORIDATION PLANT
DESERT CENTER, CALIF.

For many years much research and experimentation has been done to find means of removing excessive fluoride from water from domestic use.

Many types of processes for the removal of fluoride have been established; however, most of them have not proven practial.

After the installation of the Lake Tamarisk fluoride removal plant at Desert Center, California, many months of trials and errors of experimentation resulted in an established process that ended the search for a simple and practical method of fluoride removal from domestic water.

The Lake Tamarisk pland has now been in operation for over seven years and is operating far above original expectations.

During a normal, average process run, each cubic foot of media will treat 4200 gallons of raw water.

The actual grains of fluoride remover per cubic foot of media will average 1700 grains with a high in excess of 2,000 grains per cubic foot of media.

The labor and chemical costs (including pumping costs) for producing water at the Lake Tamarisk Defluoridation Plant is nineteen cents per 1000 gallons.

The sole purpose of the Lake Tamarisk Defluoridation Plant is to change the fluoride content of well water with a fluoride level of 7.5 ppm to water with an acceptable fluoride level of 0.8 ppm or less.

The actual chemistry of removal of fluoride in this process has not been completely defined. However, it is believed to be a combination of ion exchange and adsorption.

The fluoride removal by this process is accomplished by passing raw well water through a media bed of activated alumina. (supplied by Alcoa)

As the water passes through the activated alumina bed, the fluoride ion is exchanged and trapped in the media bed. The resulting effluent is water with an acceptable fluoride level of 0.8 ppm or less.

Figure C-5. Description of process at Desert Center, California, as provided by Robert E. Anderson.

The flow through the bed can continue until such time as the alumina media is saturated to a point where there is not sufficient ion exchange and/or adsorption and the resulting effluent is above acceptable levels. At this point, the loaded media bed necessitates regeneration.

The regeneration process is preceded by first cleansing the media bed of foreign matter such as fine silts and iron oxides that accumulate on top of the bed during the process run. This is done by an up-flow rinse of raw water through the bed. No addition of chemicals is needed at this point.

Regeneration consists of passing a solution of Sodium Hydroxide (NaOH) through the media bed for a required length of time. During this regenerate period the release of fluoride by the activated alumina is immediate. However, to remove the released fluoride from the bed requires a bed neutralization rinse.

The neutralization rinse continues until such time as the effluent fluoride level has dropped to a required range. The effluent flow can then be turned into the potable water supply. (reserviors, etc.)

After the regeneration process and during the process run, PH control of the raw water is very important. This is accomplished by installing a chemical injection point in the raw water influent line prior to entering the media.

The pH control of the treated water effluent may or may not be a factor. In any event, this also is easily controlled by injection of the proper chemical in the treated water effluent prior to entering storage reserviors, etc.

Raw water pH control is continued through out the process run until the activated alumina bed is again saturated with fluoride and the fluoride removal is insufficient. At this point the production cycle is ended and another begins.

These cycles consist of four parts, namely: Pre-regenerate rinse, passing of the regenerate fluid through the media bed, bed neutralization rinse and the process run.

Submitted by:

Robert E. Anderson
P.O. Box 495
Desert Center, California

Figure C-5. (continued)

4. Media Neutralization

   a. Media bed is washed with water at 2.5 to 3.0 pH at 1,100 to 1,300 liters per min (300 to 400 gpm) for 1.5 hr (S.V. = 0.0011 to 0.0014 $sec^{-1}$, or residence time of 15 to 11.2 min).
   b. Acid used to lower pH is sulfuric ($H_2SO_4$).
   c. Secondary washing is with water at ~4.0 pH, to extent of ~380 $m^3$ (~100,000 gal).

TO: R. Shaver, R. Smith, E. Juergens

FROM: I. Frankel

Date: 14 June 1976

Subject: Trip Report, Visit to Alumina Treatment Plant, Bartlett, Texas 5/25/76

Contact: Mr. Billy White
Utilities Superintendent
(817) 527-3557

Bartlett, Texas, is a small community, approximately 72 km (45 mi) south of Waco. The community's water supply is obtained from deep wells and is potable as pumped except for fluoride content. The well water presently obtained has a fluoride content of only 3.0 ppm of $F^-$. However, when the alumina treating plant was first constructed (1949), the well in use at that time produced water having an 8 ppm $F^-$ content.

The treatment is quite simple. Untreated well water passes by gravity through a bed of media (Alcoa F-1 activated alumina, 28 to 48 mesh). The fluoride content is reduced to an average of ~1 ppm of $F^-$ and is pumped to storage without additional treatment.

The treatment tank is constructed of steel but is coated on the inside with a durable organic coating ("Vinoline" from TNEMEC Co., North Kansas City, Missouri). The coating is now 4 years old and is generally holding up well; it is alleged to have an 8-year life. The treatment tank is vertical (2.9 m or 9'6" high) and cylindrical (3.35 m or 11' in diameter), and thus has a total volume of 26 $m^3$ (6,870 gal). Tank drainage or backflow is handled by an X pipe grid on the bottom. This is covered by 30 cm (12 in) of graded gravel, then by an alleged 1.52- to 1.60-m or 5- to 5¼-ft bed of media. This depth is equivalent to about 1.9 $m^3$ (500 $ft^3$) of media, but I do not believe that the bed was more than ~0.9 m (~3 ft) deep on the day of my visit. There is about 0.9 m (3 ft) of free space above the media and an X-shaped launder that discharges backwash water. The tank has no cover, although it and its accessory equipment are in a fully enclosed building.

The plant handles about 680 $m^3$ (180,000 gal) of water per day; the media is regenerated every 378.5 $m^3$ ($10^6$ gal), and regeneration occurs every 4 days in summer and about once a week in winter. About 227 kg (500 lb) or

~2.3 $m^3$ (~9.1 $ft^3$) of media is added per year as make-up for miscellaneous losses.

Regeneration is accomplished by dissolving 227 liters (60 gal) of 50-percent caustic soda to 19 $m^3$ (5,000 gal) of solution (0.9-percent) and flowing this selection by gravity through the media. The bed is then backwashed using 76 $m^3$ (20,000 gal) of well water. Washing is continued using 151 $m^3$ (40,000 gal) on a gravity flow basis. Acid washing by gravity flow removes final traces of free caustic [295 kg or 650 lb of 93-percent sulfuric acid is added to sufficient water to make 1,830 kg or 4,030 lb (~1,665 liters or ~440 gal) of 15-percent acid, which in turn is diluted to 19 $m^3$ or 5,000 gal of ~1.5-percent acid]. The acid is washed out with 151 $m^3$ (40,000 gal) of well water by gravity flow at a rate of ~1.14 $m^3$ per min (~300 gpm). All waste streams are sewered, and the sewage plant overflows to a normally dry river bed.

Analyses of water samples were allegedly done with a Klett-Summerson spectrophotometer. However, this instrument was so dusty and so obviously unusable that the writer doubts that routine analyses are performed. Infrequent state water analyses are probably the basis for water quality judgments.

Labor application on the plant is stated to be about 0.5 man-days per regeneration. Costs of operating the plant were 2¢/1,000 liters (8¢/1,000 gal) about 10 years ago, but they are not now known. Based on chemical usage and labor required for regeneration only, processing costs are calculated by the writer at:

| | |
|---|---|
| 0.008¢/1,000 liters ($0.0318/1,000 gal) | - chemicals, including media make-up |
| 0.005¢/1,000 liters ($0.0206/1,000 gal) | - labor for regeneration |
| 0.014¢/1,000 liters ($0.0524/1,000 gal) | - processing costs, not including maintenance, depreciation, and power |

TO: 489 Distribution

FROM: I. Frankel and E. Juergens

Date: 25 May 1976

Subject: Initial Visit to Feldspar Corporation, Spruce Pine, North Carolina, May 20-21, 1976

Plant Contacts: Larry Sparks, Research Director
Richard Barber, Vice President
Charles Wiseman

This memo summarizes information obtained by discussions between Versar representatives and Feldspar personnel with regard to current operations and intentions for the future operations at the Spruce Pine facility.

Feldspar Corporation currently employs an Orion specific ion meter (Model No. 407A) in conjunction with a fluoride combination electrode (Orion Model No. 96-09) for fluoride determinations. Double concentration total ionic strength adjustment buffer (TISAB) is utilized to negate possible interference caused by the presence of aluminum ($Al^{+3}$) and/or ferric ($Fe^{+3}$) ions.

The influent to feldspar flotation conditioning is approximately 1,135 liters per min (300 gpm). The pH at this point is 2.5 to 3.0, and conditioning time is about 2 min. Conditioning reagents added at this point are HF, oleylamine acetate (Alamac IIC-General Mills), polypropylene glycol, and a trace amount of sulfuric acid. Upon occasion, fuel oil is added at pump boxes to reduce clogging throughout the system. Sulfonated white oil may be present as a result of carryover from the previous flotation process. Fluoride concentration is ~100 to 150 ppm. Feldspar Corporation indicated that further analysis and characterization such as suspended solids, total solids, etc. would be performed and results would be forwarded to Versar.

The effluent from feldspar flotation is separated into two portions, each with a flow of 570 liters per min (150 gpm)--sand underflow and feldspar float. After respective sand and feldspar removal, the effluents are recombined. The recombined stream is expected to contain some of the above mentioned conditioning reagents and a significant amount of floating/suspended solids--most of which are 80 to 200 mesh feldspar.

Total plant effluents are currently combined and treated with lime (hydrated lime, Williams Lime Co.) until a pH of 9.5 to 10 is reached. The purpose of lime treatment of total plant effluent is to elevate the pH to the desired discharge level and to act as an aid to flocculation. At the point of discharge, the flow is ~7,600 liters per min (~2,000 gpm). At present, lime treatment does not promote calcium fluoride precipitation.

If Versar's research and development effort on effluents from the feldspar-sand flotation (separation) step is successful, process wastewaters from each stream (sand underflow water and feldspar float water) would be combined. The combined streams from each of two adjacent plants would also be combined, resulting in a total flow of 2,270 liters per min (600 gpm) of fluoride-containing water. An expected 50 percent of this water can be recycled directly to the flotation units with no treatment. Unfortunately, recycling results in an eventual buildup of flotation reagents to unacceptable levels. It is therefore necessary to purge a fraction of the recycling water, in this case up to a maximum 1,135 liters per min (300 gpm) for both plants. This is the stream that would require defluoridation.

Since fluoride-containing wastewaters would be at a pH of 2.5 to 3.0 (below the range needed for effective removal of fluoride by activated alumina), liming would be required at this point. If calcium fluoride precipitation is desirable, it would require sufficient liming to raise the pH above 9. The necessity for calcium fluoride precipitation has yet to be determined. There is a recognized necessity to pretreat activated alumina destined wastewater to remove or significantly reduce the amount of floating/suspended feldspar for the elimination of clogging of the activated alumina.

Mr. Sparks' research gave evidence that fluoride ions are adsorbed on the feldspar (floating/suspended) to further complicate the effective removal of fluoride. It was concluded that removal of this feldspar from the effluent is both functionally necessary and economically desirable.

Feldspar Corporation's mode of operation is alleged to be similar enough to other existing feldspar operations that a system designed for Feldspar Corporation could be readily adopted by the rest of the industry.

APPENDIX D. COST ESTIMATE WORK SHEETS

Cost of Chemicals, 1977 Prices

1. Activated Alumina (media)

Assume: 163,000 kkg/year (180,000 tons/year) feldspar production
1,135 liters per min (300 gpm) flow - process wastewater (PWW)
4-min residence time on media
2 columns of media - in parallel
833 to 881 kg/$m^3$ (52 to 55 lb/$ft^3$) - bulk density of media
66¢/kg (30¢/lb) - cost of media, delivered
7.48 - gal/$ft^3$
48 volumes PWW containing 60 ppm $F^-$ to exhaust 1 volume media
1.75 to 2.25 hr to regenerate media (use 2.5 hr)

$$\frac{300 \text{ gpm}}{48} \mid \frac{60}{} \mid \frac{2.5}{7.48} = 3.54 \text{ m}^3 \text{ (125 ft}^3\text{) media/column - this is design basis for column}$$

(125) (2) (55 lb/$ft^3$) ($0.30/lb) = $4,125 = initial investment for alumina

Experience factor for alumina make-up at Desert Center, California, and Bartlett, Texas, is ~15 percent per year. However, for continuous media use, use 100 percent replacement per year.

$$\frac{\$4{,}125}{180{,}000 \text{ tons/year}} = \$0.0252/\text{kkg (\$0.0229/ton) feldspar}$$

2. Lime

Cost of lime is $63.40/kkg ($57.50/ton), delivered, including sales tax.
Lime usage is ~0.1 g/liter (834 x $10^{-6}$ lb/gal) for initial removal of $F^-$ from wastewater.

$$\frac{0.000834 \text{ lb}}{\text{gal}} \mid \frac{300 \text{ gal}}{\text{min}} \mid \frac{60 \text{ min}}{\text{hr}} \mid \frac{24 \text{ hr}}{\text{day}} \mid \frac{6 \text{ day}}{\text{week}} \mid \frac{52 \text{ weeks}}{\text{year}} \mid \frac{\text{year}}{180{,}000 \text{ tons}} \mid \frac{\$57.50}{2{,}000 \text{ lb}} =$$

$0.0198/kkg ($0.0180/ton) spar = cost of lime

3. Calcium Chloride

Cost of calcium chloride is ~$25/kkg (~$23/ton), fob manufacturer
Assume: $33/kkg ($30/ton) delivered, as 40 to 45 percent solutions.

Use is $\frac{0.45 \text{ g}}{\text{liters PWW}} \mid \frac{3.785}{454} = 0.45$ g/liter (0.00375 lb/gal) PWW

$$\frac{0.00375}{} \mid \frac{300}{} \mid \frac{1{,}440}{} \mid \frac{312}{180{,}000} \mid \frac{\$30.00}{2{,}000} = \$0.0464/\text{kkg (\$0.0421/ton) for PWW pretreatment}$$

Calcium chloride is also used to remove $F^-$ from regenerant caustic.

$$\frac{125\ ft^3}{} \left| \frac{2.5\ volumes}{volume} \right| \frac{62.4\ lb}{ft^3} \left| \frac{600 \times 10^{-6}}{} \right. = \text{5.3 kkg (11.7 lb)} F^- \text{ to be removed every 2.5 hr}$$

19 = atomic weight of $F^-$
111.1 = molecular weight of $CaCl_2$

If we use 1.2 times stoichiometric values of $CaCl_2$ for $F^-$, and if $F^-$ concentration averages about 600 ppm, then

$$\frac{11.7}{} \left| \frac{111.1}{19 \times 2} \right| \frac{24}{2.4} \left| \frac{312}{} \right| \frac{\$30}{2,000} \left| \frac{1.2}{180,000} \right. = \$0.0114/kkg\ (\$0.0103/ton)$$

The sum of PWW pretreatment and fluoride removal from regenerant is

$$\begin{array}{r} \$0.0103 \\ +0.0421 \\ \hline \$0.0524 \end{array}$$

$0.0578/kkg or $0.0524/ton = $CaCl_2$ costs

4. Caustic Soda

Assume that soda is purchased as a 50-percent solution, 76 percent $Na_2O$ basis. Recent quote is $154 to $192/kkg ($140 to $175/ton), fob works, freight equalized (C.M.R.).

Assume that cost is $176/kkg ($160/ton) delivered.

Lab data required 2.5 volumes of 1-percent NaOH/volume of media every 2.5 hr

$$\frac{125\ ft^3}{} \left| \frac{2.5\ volumes}{volume} \right| \frac{62.4\ lb}{ft^3} \left| \frac{.01}{} \right. = 88.5\ kkg\ (195\ lb)\ NaOH/2.5\ hr$$

$$\frac{195}{2.5} \left| \frac{24}{} \right| \frac{312}{} \left| \frac{\$160}{2,000} \right| \frac{}{180,000} = \$0.2862/kkg\ (\$0.2596/ton)$$

5. Sulfuric Acid

Use 5 volumes/volume of acidulated water per regeneration, discharging 50 percent of it after each cycle. Prepare acidulated water by adding 5 volumes natural water to 1 volume 1 percent $H_2SO_4$.

$$\frac{125\ ft^3}{} \left| \frac{2.5\ volumes}{volume} \right| \frac{7.48\ gal}{ft^3} \left| \frac{8.34\ lb}{gal} \right| \frac{24}{2.5} \left| \frac{312}{} \right| \frac{1}{6} \left| \frac{.01}{} \right| \frac{\$40}{2,000} \left| \frac{}{180,000} \right. =$$

$0.0119/kkg ($0.0108/ton) acid cost

Labor and Supervision

The rate of pay at Spruce Pine is ~$265/week. This rate includes benefits, fringes, overhead, and average overtime. Equivalent supervisory costs are $30/week.

Assume that one operator per shift is required (may be somewhat less than this with proper process instrumentation).

∴ Use three operators per day with supervisor for a total of approximately $300/week per operator

$$\frac{\$300 \mid 3 \mid 52}{\mid \mid 180{,}000} = \$0.29/\text{kkg}\ (\$0.26/\text{ton}) = \text{labor and supervisory cost}$$

Equipment Calculations

1. Activated Alumina Column

$3.54\ m^3$ ($125\ ft^3$) media

$\frac{\pi}{4}(D^2)(H) = 125$

let $D^3 = H$

$$D = \frac{125 \mid 4}{\mid \pi} = 159+$$

D = ~1.64 m (~5.4 ft) = 165 cm (65 in)

Use 80 percent free space above media for backwashing. Add 0.3 m (1 ft) below media support for liquid collection.

∴ Media columns are 1.64 m (5.4 ft) I.D. and 3.26 m (10.7 ft) high.

2. 50-percent Caustic Storage Tank

$$\frac{125 \mid 2.5 \mid 7.48 \mid 8.34 \mid .01 \mid 24 \mid 6 \mid 30}{\mid \mid \mid \mid \mid 2.5 \mid 7 \mid} = 21{,}800\ \text{kg}\ (48{,}100\ \text{lb})\ \text{NaOH/month}$$

1.53 = specific gravity of 50 percent caustic

(χ gal) (1.53) (8.33) = 21,800 kkg (48,100 lb)/month

χ = 14,300 liters (3,780 gal) 50-percent caustic regenerated per month

∴ Plan on 15,000-liter (4,000-gal) tank.

3. 1-percent Caustic Storage Tank

$$\frac{125\ ft^3 \mid 5.0\ \text{volumes} \mid 7.48}{\mid \text{volume} \mid} = 13{,}700\ \text{liters/cycle}\ (4{,}675\ \text{gal/cycle})$$

∴ Plan on 19,000-liter (5,000-gal) storage tank.

4. Acidulated Water Storage Tank

Use same size tank as for 1-percent caustic: 19,000 liters (5,000 gal).

5. Regeneration liquor treatment tank

$$\frac{125 \mid 2.5 \mid 7.48 \mid 6\ \text{hr}}{\qquad\quad \mid \qquad \mid 2.5} = 21{,}300\ \text{liters (5,610 gal)}$$

Use 22,700-liter (6,000-gal) tank with bottom outlet for calcium fluoride slurry, carbon steel, coated.

6. PWW In-line Mixing Tank, Agitated

1,135 liters per min (300 gpm) PWW flow

Use 3,785-liter (1,000-gal) tank for 3+ min residence, with agitation.

7. Calcium Chloride Storage Tank

Assume 40-percent concentration of purchased calcium chloride
Specific gravity = 1.47 for 40-percent solution

$$\frac{0.00375\ \text{lb}\ CaCl_2 \mid 300\ \text{gpm} \mid 1{,}440\ \text{min} \mid 26\ \text{day} \mid \qquad\qquad}{\text{gal PWW} \mid 0.4 \mid \text{day} \mid \text{month} \mid 8.33 \times 1.47} = 32{,}500\ \text{liters per month (8,600 gal/month) of 40-percent } CaCl_2 \text{ regenerated}$$

$$\frac{11.7\ \text{lb}\ F^- \mid 111.1 \mid 24 \mid 26 \mid \qquad \mid \qquad \mid \qquad}{\text{cycle} \mid 19 \times 2 \mid 2.5 \mid \qquad \mid .40 \mid 8.33 \mid 1.47} = 6{,}600\ \text{liters (1,743 gal) of 40-percent } CaCl_2\text{/month for regenerant liquor}$$

$$\begin{array}{r} 8{,}600 \\ 1{,}740 \\ \hline \end{array}$$

Total - 10,340 gal/month or 39,140 liters per month

Purchase 42-$m^3$ (11,000-gal) tank for monthly filling of 40-percent $CaCl_2$ tank. Carbon steel OK; could use Haveg, special concrete, etc.

8. Treated PWW Settling Tank

Use 30 to 35 min settling time. Bottom slightly conical, with bottom slurry discharge.

1,135 liters per min (300 gpm) (35) = 40-$m^3$ (10,500-gal) tank.

Vacuum Disc Filter Cost

$$(10^{-6})\ (160\text{-}5)\ (300\ \text{gpm})\ (8\text{-}33)\ (1{,}440)\ \left(\frac{78}{38}\right) = 340\ \text{kg/day (750 lb/day) of } CaF_2$$

As 50 percent cake, would be ~454 kg/day (~1,000 lb/day)
w/e = (2) (63) = 2,020 kg/$m^3$ (126 lb/$ft^3$)

$\frac{1,000}{126}$ = 0.23 $m^3$/day (8 $ft^3$/day)

Assume 0.09 $m^2$ (1 $ft^2$) discs, with 5-cm (2-in) cakes on both sides of a disc.

| | thick | sides | discs | cycles/day |
|---|---|---|---|---|
| (8 $ft^3$) = | ($\frac{2 \text{ in}}{12}$) | (2) | (5) | X |

3 cycles/day = X

($550/ft) (10 lb/$ft^2$) ($\frac{195}{125.7}$) (1.65) = $14,600

per $ft^2$ in 1970 — index adj. — installing tanks

Calcium Fluoride Credit

($10^{-6}$) (160-5) (300) (8.33) (1,440) (312) ($\frac{78}{38}$) ($\frac{\$70}{2,000 \text{ lb}}$) ($\frac{1}{180,000}$)

$0.0519/kkg ($0.0471/ton) of feldspar

Credit not taken at this point because of uncertainty of market.